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# Journal of Polymer Science, Part B

# Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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Journal of Polymer Science **Part B: Polymer Letters**

**Editorial Board:**
R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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# EFFECT OF POLYMERIZATION TIME ON THE MOLECULAR WEIGHT DISTRIBUTION OF LOW PRESSURE POLYETHYLENE

Low pressure polyethylene prepared by heterogeneous polymerization has been found to have an unusually broad molecular weight distribution (1-3). To study the manner by which the molecular weight distribution varies during the course of polymerization, we have determined the molecular weight distribution of low pressure polyethylene as a function of polymerization time. A typical Ziegler-type catalyst system used was a mixture of 2.5 millimoles of titanium tetrachloride and 1.25 millimoles triisobutylaluminum per liter of high purity n-heptane. Usual precautions were taken to exclude oxygen and moisture in the polymerization system. After the desired time of polymerization at 25°C. the reaction was quenched by the addition of ethanol. A batch fractionation technique was used to determine the molecular weight distribution. Molecular weights of the fractions were obtained from inherent viscosities determined in Tetralin at 130°C. using the relationship (4)

$$[\eta] = 4.6 \times 10^{-4} \times M^{0.725}$$

The inherent viscosity at 0.1 g./100 ml. concentration was taken as the intrinsic viscosity $[\eta]$ in the above equation.

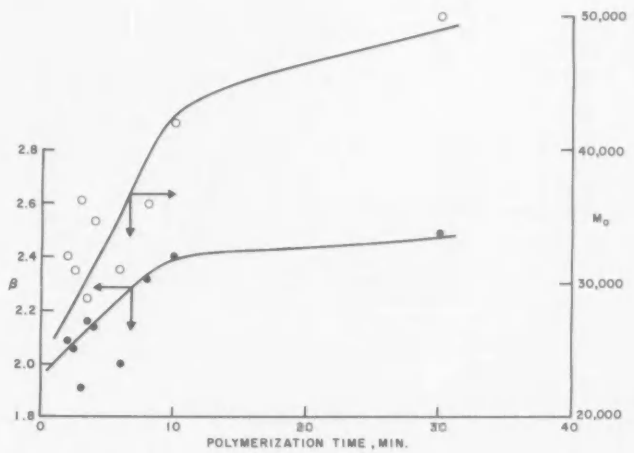


Fig. 1. Molecular weight distribution parameters, $\beta$, $M_0$, vs. polymerization time.

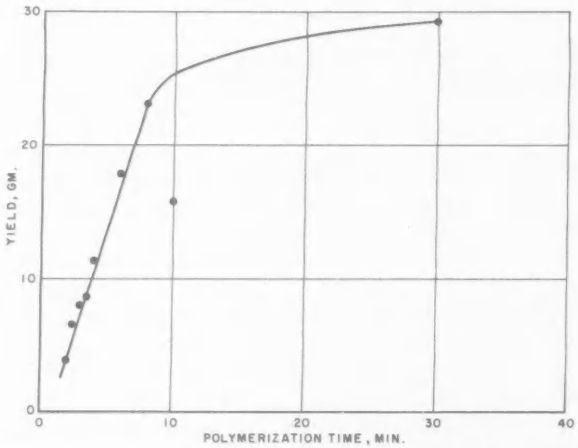


Fig. 2. Yield vs. polymerization time.

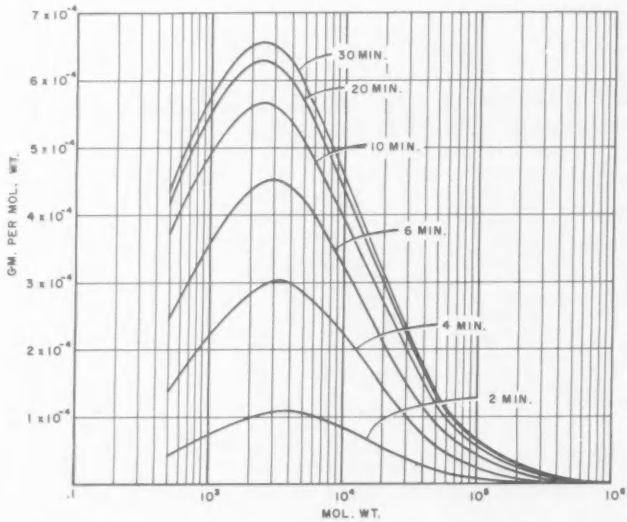


Fig. 3. Molecular weight distribution at various polymerization times.

The molecular weight distribution of all samples was found to follow the Wesslau distribution function (1)

$$W(M) = (1/\beta\sqrt{\pi})(1/M)\exp\{-(1/\beta^2)\ln^2(M/M_0)\}$$

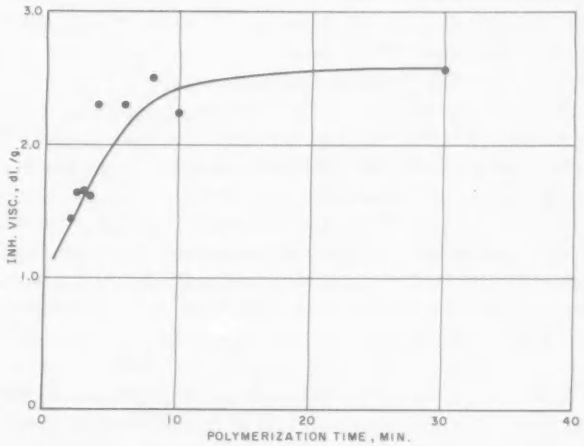


Fig. 4. Inherent viscosity vs. polymerization time.

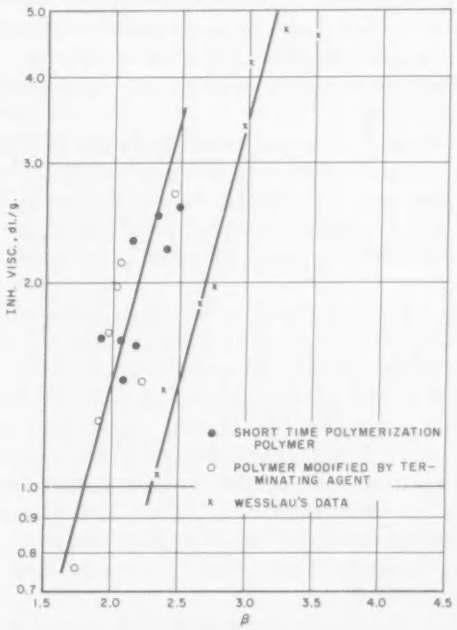


Fig. 5. Molecular weight distribution parameter $\beta$ vs. inherent viscosity.

Where W(M) is the differential distribution function, and $M_0$ and $\beta$ are two adjustable parameters ($\beta$ is related directly to the breadth of molecular weight distribution). Figure 1 shows the variation of $\beta$ and $M_0$ with polymerization time. The parameter $\beta$, even though increasing with polymerization time, is fairly high at the shortest polymerization time. At this time, the weight- to number-average molecular weight ratio calculated from $\beta$ is already as high as nine, thus agreeing with Wesslau (5) that broad molecular weight distribution polymer is produced at the very beginning of the polymerization.

The yield versus polymerization time is shown in Figure 2. It is seen that although the molecular weight distributions do not show a steady state polymerization, the rate of polymerization was constant between 2 and 8 min. Constant polymerization rate was observed by Badin (6) for ethylene polymerization and by Natta (7) for propylene polymerization.

Figure 3 shows the change of molecular weight distribution with polymerization time. The relative magnitude of the differential distribution curves is based on the smoothed value of the yield versus polymerization time relation shown in Figure 2. Molecular weight is plotted on a logarithmic scale. The smoothed values of $\beta$ and $M_0$ from Figure 1 were used to calculate the curves. It can be seen that the maxima of the distribution curves do not increase with polymerization time. The broadening of molecular weight distribution was brought about by the simultaneous increase of both very low and very high molecular weight chains with polymerization time.

Figure 4 shows that the average molecular weight (indicated in the plot by inherent viscosity) increases with polymerization time. This observation is in agreement with that of Chien (8) for ethylene polymerization and that of Natta (7) for propylene polymerization. The polymerization reactions of the present system therefore must not be in a steady state.

Shown in Figure 5 is a plot of $\beta$ versus the logarithm of inherent viscosity. The open circles in the plot represent the $\beta$ of polymers produced in normal polymerization time but with a termination agent added to the monomer to control the molecular weight. The variation of $\beta$ with inherent viscosity follows roughly the same line for both polymers. Gordon and Roe (9) derived from a surface-chemical mechanism, a function for low pressure polyethylene molecular weight distribution which resembled the distribution observed in experiments. Based on such a mechanism, Roe (10) deduced that a termination agent would bring about a narrowing of molecular weight distribution. The results shown in Figure 5 contradict Roe's deduction.

Wesslau (1) also observed a variation of $\beta$ with average molecular weight. The crosses in Figure 5 are Wesslau's data after conversion to the units used in the present work. The distribution of Wesslau's poly-

mer is broader. The variation of $\beta$ with inherent viscosity is similar to that of the polymers studied in the present work, as indicated by the parallel lines in Figure 5.

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# THE STEREOSPECIFICITY OF TRIMETHYL LEVOGLUCOSAN POLYMERIZATION*

In previous papers of this series the polymerization of various 1,6-anhydro sugar derivatives has been reported (1-4) and the greater ease of polymerization of those 1,6-anhydro sugars having a free hydroxyl group on the 2 position has been noted (3,4). Recently Russian workers have found conditions under which trimethyl levoglucosan (1,6-anhydro-2,3,4-trimethyl-$\beta$-D-glucopyranose) will polymerize to products of $\eta_{sp}/C$ = 0.22 to 0.30 (unspecified concentration) and molecular weight by light scattering of 280,000 to 394,000. We wish to confirm the significant observation that boron trifluoride etherate in toluene does produce polymers from trimethyl levoglucosan of about this viscosity and to add a few further observations.

The very high molecular weights obtained by the Russian workers by light scattering probably reflects the presence of microgel in their preparations as has been observed on other polysaccharides (1,2,6). Number average degrees of polymerization on our ether-insoluble products ranged up to 25 at similar viscosity levels and no other explanation presents itself for the abnormal weight average molecular weights they observed.

The yield of ether-insoluble polysaccharide (around 90%) was relatively insensitive to the addition of water. Polymerization occurred more slowly, but 65% of ether-insoluble product was formed even when there was added a catalyst mixture containing one half a mole of water per mole of boron trifluoride. In addition an ether-soluble product of degree of polymerization of about eight was formed in these polymerizations.

The Russian workers reported the optical rotation of unsubstituted levoglucosan polymers and their values as expected indicate a mixture of $\alpha$ and $\beta$ forms. They noted the crystallinity of the trimethyl levoglucosan polymers, but did not report their rotation. We have found that the rotation of these products is very high, $[\alpha]_D$ = 197-199°, indicating an overwhelming predominance of $\alpha$ linkages. The polymers produced somewhat more slowly in the presence of water or (especially) isopropyl alcohol have even higher rotations increasing regularly with increase in water content to $[\alpha]_D$ = 203-204°. This can not reflect the concomitant decrease in molecular weight which, of course, has the opposite effect. Clearly this polymerization is under steric control of the catalyst complex and a decrease in rate is accompanied by an increase in the steric control. This result is quite analogous to the "proliferous" and "flash"

*Addition Polymerization of Anhydro Sugar Derivatives. VI.

TABLE I

Polymerization of Trimethyl Levoglucosan

| No. | Monomer conc., g./100 ml. | $BF_3$-etherate/ Monomer mol ratio, % | $H_2O/BF_3$-etherate mol ratio, % | Duration, hr. | Time of gel form, min. | Yield ether-insolubles, g. from 2 g. | M.P. | $[\eta]$ | D.P. | $[\alpha]_D^{25}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| P 9 | 30 | 24 | 0 | 45 | <5 | 1.8 | 272-5 | 0.17 | 25 | +197 |
| P 10 | 15 | 24 | 0 | 45 | <5 | 1.8 | 262-5 | 0.15 | 24 | +199 |
| P 1 | 30 | 8 | 0 | 48 | <5 | 1.8 | 263-5 | 0.14 | 14 | +195 |
| P 2 | 30 | 8 | 6.3 | 45 | <5 | 1.8 | 261-5 | 0.13 | 13 | +196 |
| P 3 | 30 | 8 | 24 | 45 | 10 | 1.7 | 262-7 | 0.13 | 13 | +199 |
| P 4 | 30 | 8 | 37 | 44 | 20 | 1.6 | 260-4 | 0.12 | 12 | +200 |
| P 5 | 30 | 8 | 50 | 44 | 30 | 1.3 | 262-5 | 0.12-0.11 | 11 | +203 |
| P 8 | 30 | 8 | 25[a] | 45 | <5 | 1.8 | 265-8 | 0.11 | 14 | +204 |
| P 0 | Crystals from ether-solubles combined runs | | | | | | 241-4 | – | 8 | +162 |

[a]Isopropyl alcohol /$BF_3$-etherate; not water

polymerization of epoxides described by Schildknecht.

## Experimental

Polymerization of 1,6-anhydro-2,3,4-tri-O-methyl-$\beta$-D-glucopyranose: Trimethyl levoglucosan (m.p. 63-64°C., $[\alpha]_D^{20} = -63.7°$) was dissolved toluene in a narrow-necked tube (15 × 18 mm.). The solution was degassed by freezing and evacuation. Catalyst solution was introduced with a small syringe through a rubber sealing cap, the tube rapidly sealed, and the mixture allowed to stand at room temperature for a period of time. In all the experiments described in Table I, solution set to a solid gel. The polymer was removed from the tube, washed thoroughly with ether and dried in vacuo. Ether washings were combined, and allowed to evaporate. Ether-soluble product crystallized from solution.

Number average molecular weights were determined in a vapor pressure osmometer (Model 301A Mechrolab, Inc., Mountain View, California) using trimethyl levoglucosan as standard and chloroform as solvent at concentrations of four to eight grams per 100 ml.

Optical rotations $[\alpha]_D^{25}$ were determined in chloroform at concentrations of 0.63 g./100 ml. for the ether-soluble polymer and about 3 g./100 ml. for the ether-insoluble material.

This investigation has been supported by research grant RG-6168 from the Division of General Medical Sciences, National Institutes of Health.

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# DIFFERENTIAL THERMAL ANALYSIS OF HIGH POLYMERS
## VII. SOME LOW-TEMPERATURE TRANSITIONS

Many high polymers undergo transitions at low temperatures. Transitions involving the onset of chain-segment motion (glass transition), ordering (crystallization), and disordering (melting), etc., have been observed. The DTA cell assembly discussed in a previous paper (1), because of its small size and ease of handling, is especially convenient for the low-temperature experiments. Transitions in polytetrafluoroethylene, atactic polypropylene, and polydimethylsiloxane have been studied.

Low-temperature experiments can be easily carried out with the small cell assembly inside a metal or glass Dewar flask. Temperatures as low as −195°C. can be conveniently obtained by cooling the assembly with liquid nitrogen. A glass or metal tube wound with a heating cord or tape may serve as the heater.

Polytetrafluoroethylene (DuPont's Teflon) displays a unique first-order transition near 20°C., followed by a subsidiary transition at about 30°C., as shown in Figure 1. X-ray diffraction studies have indicated

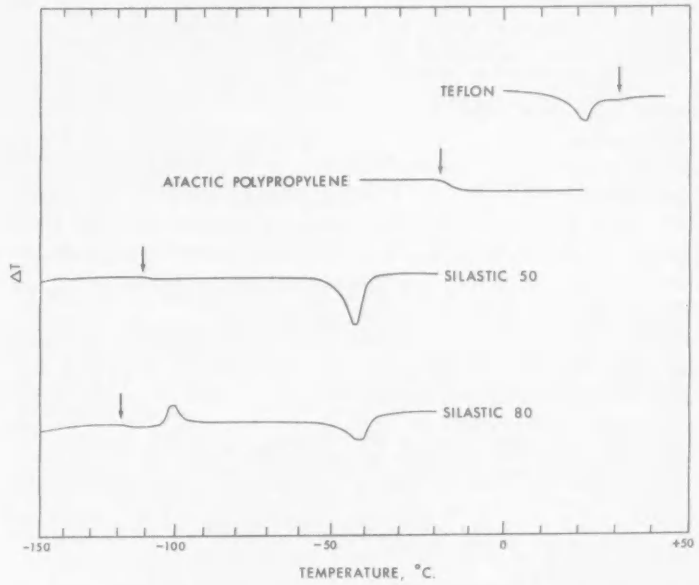


Fig. 1. Some transitions in Teflon, atatic polypropylene, and silicone rubbers at low temperatures.

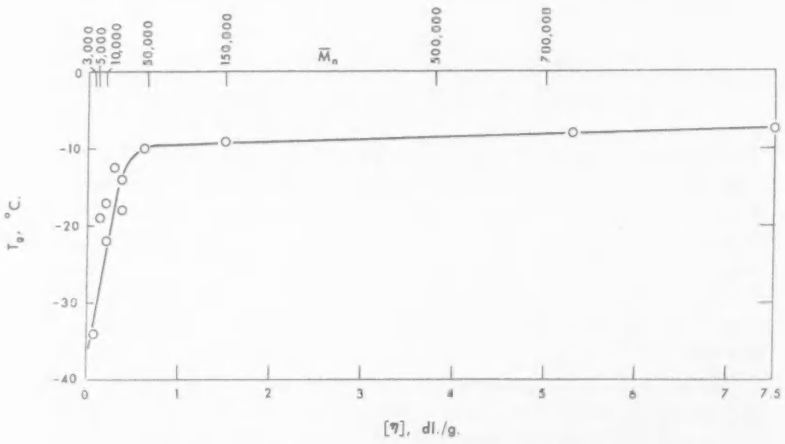


Fig. 2. Glass-transition temperature of atactic polypropylene as a function of molecular weight.

that these transitions occurring far below the melting point (327°C.) actually involve a partial disordering of the crystalline region (2). The disordering has been attributed to either longitudinal translation along, or angular displacement about, the chain axis. Evaluation of the polytetrafluoroethylene thermogram showed that the heat of the 20°C. transition, about tenfold that of the subsidiary one at 30°C., is in good agreement with other calorimetric results (3).

Polypropylene is known to have a brittleness temperature not too far below 0°C. In Figure 1, the thermogram of an atactic polypropylene with an intrinsic viscosity of 0.37 dl./g. shows a baseline inflection at −18°C., corresponding to the glass-transition temperature. The glass-transition temperature of an isotactic polypropylene with unspecified molecular weight or crystallinity has recently been reported to be −20°C., as measured by linear dilatometry (4).

In atactic polypropylene, the glass-transition temperature is expected to vary with molecular weight. This was confirmed by measuring the inflection temperatures of the thermograms of a number of atactic polypropylene samples covering a broad molecular weight range. Intrinsic viscosity of polypropylene samples was measured in decalin at 135°C. The number-average molecular weight was calculated from the equation (5):

$$[\eta] = 1.58 \times 10^{-4} \bar{M}_n^{0.77}$$

The inflection temperatures plotted against $[\eta]$ or molecular weight, as shown in Figure 2, shows a relationship typical of many other polymers

(6). Some of the samples used here may contain a small amount of crystalline material; however, its effect on the glass-transition temperatures is probably small. For instance, the atactic polypropylene with intrinsic viscosity of 5.3 was found to be 12% crystalline by x-ray analysis (7).

Two commercial polydimethylsiloxane elastomers—Dow Corning's Silastic 50 and 80—both vulcanized and containing fillers, were heated from −150°C. at a rate of 2°C./min. Polysiloxane elastomers are known to have very low glass-transition temperatures, which are attributed to the extremely flexible silicon-oxygen backbone chain. Silastic 50 had a glass transition at −112°C.; Silastic 80 at −120° (Fig. 1). However, Silastic 80 could be supercooled, as evidenced by the exothermic crystallization peak starting at −108°C. upon heating. The crystalline state in Silastic 50 may partially contribute to the somewhat higher glass-transition temperature described above. The supercooling could be due to a number of causes: the manner of quenching, the filler content, or possibly the state of vulcanization.

In both Silastic 50 and 80, the onset of melting occurs at −55°C. and ends at −44°C. Judging from the size of the melting peaks, it may be inferred that Silastic 50 is more crystalline than Silastic 80.

The low-temperature transitions illustrated here are invariably associated with changes in mechanical properties and are usually investigated by more elaborate techniques as dilatometry or mechanical property measurements over the temperature range of interest. It is clear from these few illustrations that useful information associated with such transitions can easily be studied by the simple technique of DTA.

The author thanks Dr. E. G. Kontos of U. S. Rubber Co. for the atactic polypropylene sample with 5.3 intrinsic viscosity.

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# A NOTE ON THE GLASS-TRANSITION TEMPERATURES OF ACRYLONITRILE + STYRENE COPOLYMERS

The dependence of the glass-transition temperature, $t_g$, on the composition of block and random acrylonitrile + methyl methacrylate (AN + MMA) and styrene + methyl methacrylate (S + MMA) copolymers have already been described (1). We would like briefly, to communicate the results of an examination of random acrylonitrile + styrene (AN + S) copolymers. Interest in this system arose for two reasons.

1. Measurements of the x-ray scattering from (AN + S) copolymers, using methods previously described (1), showed a distinct break at a composition corresponding to about 80 mole % AN in the curve relating intermolecular spacing with mole composition. Average intermolecular spacing at the break was 5.3A. and showed little change with increase in the proportion of AN in the copolymer. These results will be given in more detail elsewhere.

2. Homopolymers prepared from these vinyl monomers have similar glass-transition temperatures; polyacrylonitrile, 87-98°C.; polymethylmethacrylate, 105-114°C.; polystyrene, 100°C. A minimum in the glass temperature – composition curve has been observed for (AN + MMA) and (MMA + S) random copolymers and it is interesting to know if (AN + S) random copolymers show similar behavior. An examination of the solution properties of a number of acrylonitrile random copolymers in a variety of solvent/nonsolvent mixtures has shown the nature of the comonomer to be unimportant in determining the concentration of nonsolvent at which aggregation is observed (2). From these experiments (AN + S) copolymers should, therefore, be similar to (AN + MMA) copolymers. The x-ray results, however, demonstrate that this need not be the case since the glass temperature will undoubtably be affected by the mode of packing and freedom of segmental motion of the molecular chains.

Results for a series of copolymers prepared by bulk (samples 1-10) and benzene solution copolymerization (samples 11-30) are given in Table I. Copolymerization was carried out at 60°C. using carefully distilled monomers and recrystallized azobisisobutyronitrile (AIBN) as initiator. Solutions contained 40 ml. monomers, 55 ml. benzene and 0.08 g. AIBN and were polymerized for 1-4 hr. under nitrogen. Bulk polymerizations using 50 ml. mixed monomers and 0.3 mole % AIBN were carried out in Pyrex ampoules in vacuum for 3 hr. (samples 1-6) and 75 min. (samples 7-10). Polymer compositions were determined by nitrogen analysis. Glass temperatures and densities of the films prepared from these samples were determined by the methods, and with the usual precautions given earlier (1). Figure 1 gives a plot of $t_g$ for the copolymers and a

TABLE I

| Spec. | Mole fraction acrylonitrile | $d_4^{25}$ g. ml.$^{-1}$ | $n^{25}$ | $(dn/dt) \times 10^4$ deg.$^{-1}$ | $(dn/dt) \times 10^4$ deg.$^{-1}$ | $t_g$ °C. |
|---|---|---|---|---|---|---|
| 14 | 1.00 | 1.213 | 1.5187 | 0.97 | 1.60 | 92.0 |
| 10 | .962 | 1.218 | 1.5123 | 0.90 | 1.90 | 94.0 |
| 15 | .939 | 1.196 | 1.5258 | 1.03 | 2.24 | 95.3 |
| 9 | .927 | 1.200 | 1.5233 | 0.94 | 1.96 | 81.0 |
| 16 | .913 | 1.185 | 1.5270 | 1.02 | 2.41 | 86.3 |
| 24 | .900 | | 1.5309 | 0.96 | 2.02 | 88.0 |
| 26 | .878 | | 1.5284 | 0.98 | 2.10 | 97.2 |
| 23 | .867 | | 1.5319 | 0.92 | 2.32 | 85.2 |
| 22 | .852 | | 1.5346 | 1.08 | 2.56 | 89.0 |
| 17 | .825 | 1.171 | 1.5338 | 0.86 | 3.18 | 91.7 |
| 13 | .816 | 1.173 | 1.5341 | 1.12 | 2.68 | 81.0 |
| 7 | .808 | 1.173 | 1.5366 | 0.98 | 2.64 | 98.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | .750 | 1.150 | 1.5418 | 0.87 | 2.70 | 98.0 |
| 18 | .743 | 1.152 | 1.5454 | 0.98 | 2.40 | 98.7 |
| 12 | .690 | 1.134 | 1.5495 | 1.14 | 2.80 | 98.0 |
| 19 | .672 | 1.145 | 1.5478 | 1.02 | 2.81 | 98.5 |
| 11 | .604 | 1.126 | 1.5514 | 0.86 | 3.10 | 106.2 |
| 6 | .588 | 1.121 | 1.5550 | 0.84 | 2.88 | 103.6 |
| 20 | .580 | 1.130 | 1.5533 | 1.01 | 2.90 | 103.8 |
| 21 | .469 | | 1.5615 | 1.10 | 3.56 | 104.9 |
| 5 | .460 | 1.102 | 1.5665 | 0.89 | 3.48 | 102.0 |
| 29 | .449 | | 1.5625 | 1.05 | 2.98 | 101.0 |
| 4 | .266 | 1.094 | 1.5734 | 1.04 | 3.48 | 99.0 |
| 30 | .263 | | 1.5743 | 1.22 | 3.44 | 95.4 |
| 3 | .213 | 1.093 | 1.5763 | 1.32 | 3.66 | 94.2 |
| 2 | .084 | 1.085 | 1.5822 | 1.06 | 3.68 | 95.2 |
| 1 | .061 | 1.082 | 1.5862 | 1.26 | 3.64 | 96.8 |

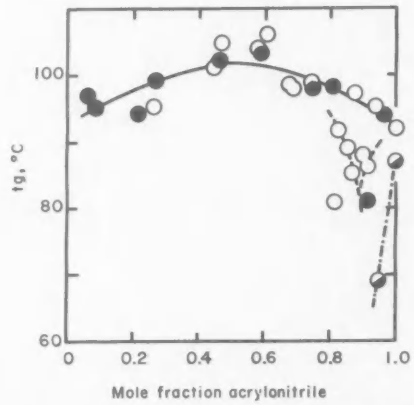


Fig. 1. The glass-transition temperature $t_g$ of random acrylonitrile + styrene copolymers prepared by bulk (●) and benzene solution copolymerization (○); results of Kolb and Izard (◕).

comparison with results obtained by Kolb and Izard (3). Repeated checks of the glass temperatures showed these to be reliable to ±0.5°C. and repeated preparations (samples 18, 19, 20, and 29) duplicated the earlier results. It was established that the results in the region 82-92 mole % AN showing a sharp minimum in $t_g$ were well outside experimental error.

The general trend shows an enhancement of $t_g$ suggestive of block copolymer properties found for (AN + MMA) copolymers (1) but also observed with acrylonitrile + vinyl acetate (4) and acrylonitrile + dimethylbutadiene copolymers (5). Other examples have been given by Kolesnikov and Avetyan (6) who examined copolymers of 1,1-dichloro-2-fluoroethylene, 1-chloro-2-fluoroethylene, and 1,1-dibromo-2-fluoroethylene with styrene, alkoxystyrenes, and methyl methacrylate. With the latter monomer a minimum glass temperature was observed whereas the styrene copolymers showed enhanced properties thus paralleling the (AN + MMA) and (AN + S) copolymers. Kolesnikov and Avetyan, loc.cit., ascribed the increase in $t_g$ to the denser packing of the polymer molecules arising from the formation of hydrogen bonds between the fluorine atoms of one chain and the hydrogen atoms of the phenyl groups on neighboring chains. Since the distribution of residues along the chain is random, such bonds will be infrequent and cause only a slight increase in $t_g$. Strong intermolecular forces exist in polyacrylonitrile and arise principally from dipole-dipole interactions between CN groups. These interactions also account for the high degree of association found in the liquid mono and dinitriles (7).

From the x-ray studies we have direct evidence that the packing in the (AN + S) copolymers is greater than in the (AN + MMA) copolymers and therefore expect the corresponding values of $t_g$ to be higher. The major part of the polymer still remains in the amorphous regions. In solution, aggregation of chain molecules is brought about by point contacts, most probably between CN groups in the case of acrylonitrile copolymers, and considerations relating to the alignment of molecular segments to form crystallites, of sufficient size to diffract x-rays, will not apply. Aggregation will then be dependent only on the proportion of acrylonitrile residues in the copolymers, provided their distribution is completely random.

The glass temperature is obviously very sensitive to the structural arrangement and packing of the chain sequences since several points in Figure 1, (sample no. 16, 17, 22, 23, and 24) show noticeably different behavior with a very sharp minimum at about 89 mole %. The only other difference between these specimens and samples 7, 15, and 26 which are of comparable composition is in the slightly greater breadth of the x-ray diffraction peak. The result of Kolb and Izard (3) gives further confirmation. There are marginal indications that polystyrene has a chain with greater flexibility than polymethylmethacrylate (1), so that when copolymerized with acrylonitrile the greater flexibility of the styrene sequences will allow the acrylonitrile residues to pack better and, of greater importance since crystallite size is known to be very small, will allow many more acrylonitrile residues to come into contact and so stiffen the whole polymer matrix. Since every attempt was made to prepare polymers under carefully controlled conditions the results of Figure 1 would suggest that for (AN + S) copolymers the balance between the intermolecular forces, causing a stiffening of the matrix, and chain flexibility can easily be shifted by slight variations in polymerization conditions and probably has its origin in changes in the distribution of sequence lengths.

Density and refractive index show a continuous change with copolymer composition and do not show a discontinuity in the region of 80-90 mole % AN. Specimens 9 and 15 for example have comparable densities although their glass temperatures differ by 14°C. The density of PAN (sample 14) was unusually high compared with the usual value of 1.184 $g.ml^{-1}$.

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# GLASS TRANSITION TEMPERATURES IN AMORPHOUS SELENIUM

The glass transition temperature, $T_g$, in amorphous selenium has been determined by a variety of techniques in the past, including thermal expansion, specific heat, and dielectric constant measurements (1), with all these results falling within the range of 29.8 ± 0.3 to 30.7 ± 0.6°C.. Recently the work was redone (2) by measurements of the specific gravity versus temperature of superpure selenium quenched from different temperatures (270, 375, and 500°C.), with the results of six determinations falling within 31.0 ± 0.5°C.. While the detailed thermal histories of the samples which were used in the determinations reported in reference (1) are not available, it seems safe to say in view of the more recent work that the quenching temperature has no appreciable effect on the transition temperature. The samples do however differ in another physical property, their tensile viscosity (2), thus showing that they do not have the same effective quench temperature which they might have acquired by re-equilibration in the cooling process. This is very surprising in view of the fact that liquid selenium at elevated temperatures represents a dynamic equilibrium between rings and chains (3) with the chain length decreasing and the polymer concentration increasing as a function of temperature, and these changes, particularly the latter, would be expected to have pronounced effects on the $T_g$ value. It means, therefore, that the lowering of the $T_g$ as a result of the decrease in chain length is exactly counterbalanced by its rise due to the increase in polymer concentration. Thus it is of interest to calculate the magnitude of these effects separately and to estimate the $T_g$ values of the pure $Se_8$ and pure polymer, which are impossible to obtain experimentally.

Effects of this type have been investigated in the past for some organic polymers. The dependence of the glass transition temperature on the molecular weight has been given by various investigators (4) in the form

$$T_g = T_g^{\infty} + A/M \qquad (1)$$

where $T_g^{\infty}$ is the value for a polymer of infinite chain length, A is a negative constant and M the molecular weight. This has been found to be particularly true for molecular weights above 5000.

The effect of added low molecular weight diluent on Tg has been discussed by Jenckel (5) who gives several relationships. Those reproducing the experimental data most accurately are

$$1/T_g = W_1/T_{g_1} + W_2/T_{g_2} \quad (2)$$

and

$$T_g = W_1T_{g_1} + W_2T_{g_2} - W_1W_2\ \Delta kn/\Delta\beta \quad (3)$$

where $T_{g_1}$ and $T_{g_2}$ are the glass transition temperatures of polymer and diluent and $W_1$ and $W_2$ the corresponding weight fractions, $\Delta kn$ is a complicated expression for the deviation from linear additivity of the refractive indices of mixtures of polymer and diluent above and below the transition temperature, and $\Delta\beta$ is a corresponding expression for the temperature coefficients of the refractive indices.

While eq. (3) seems to fit some experimental data somewhat better than eq. (2), it cannot be applied in this case due to the absence of information regarding $\Delta kn$ and $\Delta\beta$. One must, therefore, resort to eq. (2), which in conjunction with eq. (1) yields

$$1/T_g = W_1/[(A'/P) + T_{g_1}^{\infty}] + W_2/T_{g_2} \quad (4)$$

where the symbols have the meaning given above except that A/M has been changed to A′/P, since data on the chain length of selenium are available as degrees of polymerization P, rather than the molecular weight M.

The data for the glass transitions and the compositions of the samples quenched from the three temperatures mentioned above are given in Table I (2).

TABLE I

| Sample | Temperature of quenching, °K. | Wt.-% monomer | P, in units of $Se_8$ | $T_g$, °K. |
|---|---|---|---|---|
| a | 543 | 33 | 450 | 304 |
| b | 648 | 23 | 90 | 304 |
| c | 773 | 17 | 20 | 304 |

Inserting these values into eq. (4) one obtains three equations with three unknowns. Eliminating $T_{g_1}^{\infty}$ and then A′ we obtain a quadratic equation for $T_{g_2}$ which yields $T_{g_2}$ = 223 or 46°K. The second of these values must be eliminated since it yields negative values for $T_{g_1}^{\infty}$. With $T_{g_2}$ = 223, we obtain $T_{g_1}^{\infty}$ = 372°K and A′ = −940. The glass transition temperature of the pure amorphous $Se_8$ can thus be taken as −50°C. and that of the pure polymer as +(100 − 940/P)°C..

It should be pointed out that the values thus obtained are minimum values for the transition temperatures, since solutions of polymers in low molecular weight materials exhibit a lower $T_g$ in the region of intermediate composition than might be expected on the basis of eq. (2). Thus, since only the intermediate composition region is available for evaluation here, the $T_g$ values of the pure components might be expected to be somewhat higher than the calculations indicate.

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# ELECTROINITIATED POLYMERIZATION OF VINYL PYRROLIDONE

Free radicals generated at the anode of an electrolytic cell can activate polymerization of various monomers (1-3). The study of the kinetics of such reactions is frequently impeded by the coating of the electrode with insoluble material which affects the conditions of electrolysis.

Recently we reported results in a homogeneous organic system where such difficulties did not occur (4). In this present work we chose a water soluble polymer in the belief that this would yield a homogeneous aqueous system for convenience in kinetic analysis.

## Experimental

Electrolyses were performed in glass cells using platinum electrodes 1 in. × 1 in. spaced 3/4 in. apart. In all experiments vinyl pyrrolidone was dissolved in methanol containing 1.33 moles potassium acetate per liter and electrolyzed at a fixed current regulated by a constant current supply.

## Results and Discussion

Polymer formed as insoluble sheets on the anode and prevented our conducting a kinetic study. However, it was found that the physical form of this polymer was such that the resistance of the solution was unchanged and the electrolysis was not hindered.

The insoluble polymer formed at approximately 1% conversion, was collected, washed with methanol, dried, and weighed. The influence of current density and monomer concentration on the yield of polymer per faraday was determined and the data are shown in Figures 1 and 2.

Studies of the Kolbe reaction indicate that the efficiency of methyl radical dimerization increases with current density (5). Radicals which do not dimerize may initiate polymerization and the efficiency of initiation should be opposite to the tendency for Kolbe dimer formation, i.e., highest initiation efficiency at lowest current density. From Figure 2 it is evident that increase in monomer concentration leads initially to increased efficiency of electrolysis. There is however, little effect on the ratio of yield/faraday at monomer concentrations in excess of 20%. Presumably this limit is governed by the rate of diffusion of monomer to the electrode surface as well as on increased rate of termination. The absolute efficiency, however, was exceedingly low in this system and it is

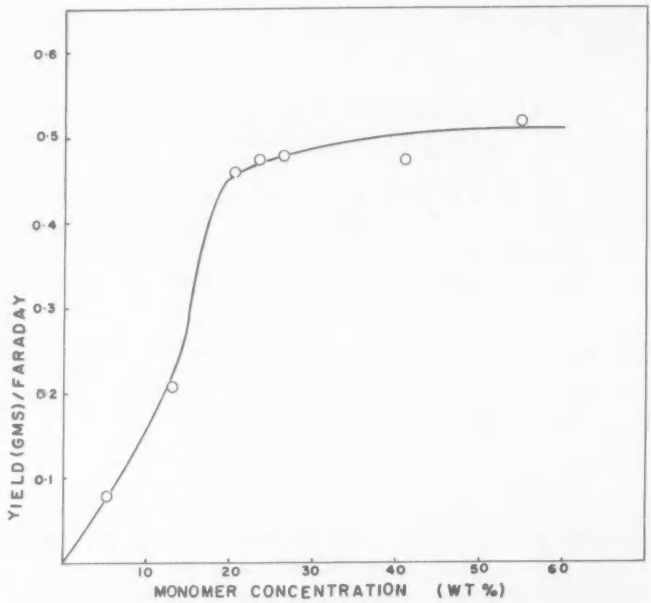


Fig. 1. Influence of current density on the weight of polymer formed per faraday.

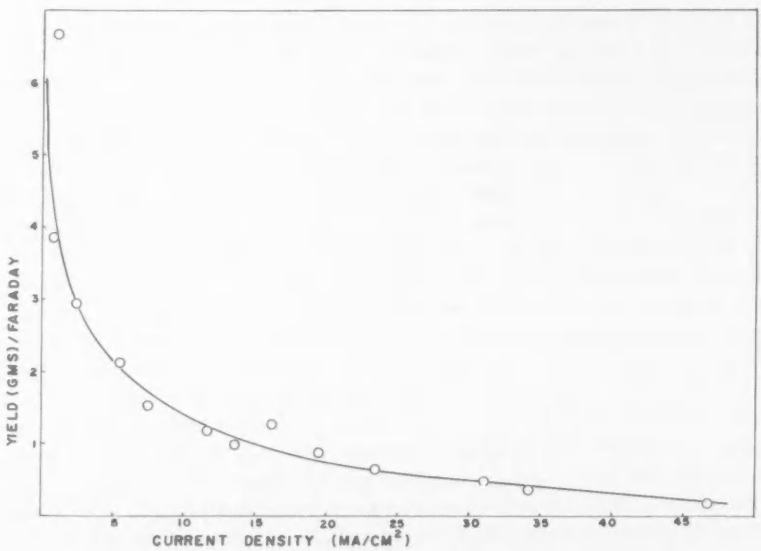


Fig. 2. Influence of monomer concentration on the weight of polymer formed per faraday.

estimated that as a maximum 0.1% of the electrons transferred ultimately resulted in the initiation of monomer.

The insolubility of the polymer formed is undoubtedly due to crosslinking. The ease of removal of labile hydrogens from polyvinyl pyrrolidone in the 3-, 5-, and $\alpha$-positions is consistent with this view. In each instance the resulting radical will possess some resonance stabilization, and in an environment of a high concentration of methyl radicals it is understandable that a predominantly insoluble polymer will form.

We gratefully acknowledge the financial assistance of the National Research Council of Canada in support of this work.

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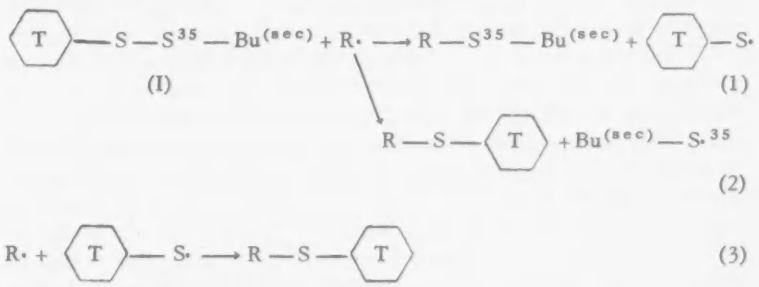
# A STUDY OF FREE RADICAL FORMATION ON IRRADIATION OF POLYISOBUTENE USING A RADIOACTIVE DISULFIDE SCAVENGER

Scavenger techniques have been widely applied to study free radical formation in radiation chemistry. In the case of saturated hydrocarbons iodine has been used to provide values of G (hydrocarbon radicals) by estimation of alkyl iodides or, equivalently, by consumption of iodine with $\gamma$-radiation or fast electrons at dose rates of up to 6 Mrad./min. (1). Because of the convenience of spectrophotometric analysis G (radical) values have been estimated mostly from the consumption of either iodine or diphenylpicrylhydrazyl, with similar results. The average of 35 such values is 6.4 with a standard deviation of 1.2 and as the range includes saturated hydrocarbons as diverse as n-hexane and 2,2,4-trimethylpentane it has been pointed out that the yield of free radicals is little dependent on details of structure (2). This generalization has even been found valid for the related yield of polymer free radicals formed by irradiation of solutions of polyisobutene in n-heptane (10 g./liter) (3,4). In all these cases studied previously the hydrocarbons were mobile and the purpose of this note is to report an extension of quantitative scavenging techniques to an exceedingly viscous hydrocarbon, a purified and thoroughly degassed polyisobutene having a viscosity of $10^9$ poise ($\bar{M}_v \sim 10^6$) at 20°C. (5).

A doubly labeled scavenger, phenyl-$H^3$-sec-butyl-$S_1^{35}$-disulfide (I) was chosen for this study because it satisfied the restrictive requirements of (1), solubility in the polymer and (2), an unequivocal scavenging role. Compound (I) scavenges a polymer radical (R·) with cleavage of the disulfide bond (6) mainly by elimination of the resonance stabilized benzenesulphenyl radical (reaction 1). Other scavenging reactions may include elimination of sec-butylsulphenyl radicals from the disulfide (reaction 2) and reaction of either benzenesulphenyl or sec-butyl-sulphenyl radicals with polymer radicals (reactions 3 and 4).



$$R\cdot + Bu^{(sec)}—S\cdot^{35} \longrightarrow R—S^{35}—Bu^{(sec)} \qquad (4)$$

The only other likely fates for the sulphenyl radicals are various radical recombination reactions since other experiments have shown that they do not react with polymer molecules under similar reaction conditions. It is permissible therefore, to equate G (combined sec-Bu-$S^{35}$ — + ⟨T⟩—S—) with G (polymer radicals).

Since the disulfide diffused very slowly, and possibly incompletely, into the polymer it was carried in with the common solvent analytical grade petroleum ether (b.p. 30–40°C.) which was subsequently largely pumped off (less than 5%, on weight of polymer, remaining) before the mixtures were sealed in evacuated pyrex tubes. Mixtures with varying proportions of disulfide were exposed simultaneously with water cooling (~20°C.) to a beam of 4 Mev. electrons from a linear accelerator at a dose rate of 1 Mrad./min. Several days later the mixtures were dissolved in toluene and the polymer recovered by precipation with methanol and centrifuging. This process was repeated three times and finally $S^{35}$ and tritium activities determined in toluene solution in a liquid scintillation counter. It is certain that the measured activities represented scavenger combined with the polymer because unirradiated controls were found to be inactive after similar treatment.

The results obtained after a dose of 1 Mrad. (Fig. 1) show that there are more $BuS^{35}$- groups than ⟨T⟩—S-groups combined with the polymer, and hence that reaction (1) assumes the predominant scavenging role except at very low concentrations of scavenger. A G (polymer radical) value of 7.3 is attained with a scavenger concentration of near $10^{-4}$ moles/g. and is not increased by using higher concentrations. At a higher dose of 5 Mrad. radical trapping was incomplete in the same concentration range, indicating some unresolved complication. However, as similar results to those in Figure 1 were obtained even at this higher dose in experiments with labeled thiophenol as scavenger it seems permissible to consider their general implications.

Comparison with results for mobile hydrocarbons indicates that a high viscosity does not reduce the yield of radicals but increases the concentration of scavenger needed to trap them by about one order of magnitude. A similarly large concentration requirement has previously been observed where scavengers have been used to suppress network formation on irradiation of another highly viscous polymer, natural rubber (7). A reasonable explanation may be developed from the generally held view that free radicals are formed in clusters, of two or more, on absorption of high energy radiation. In a viscous medium interradical reactions within clus-

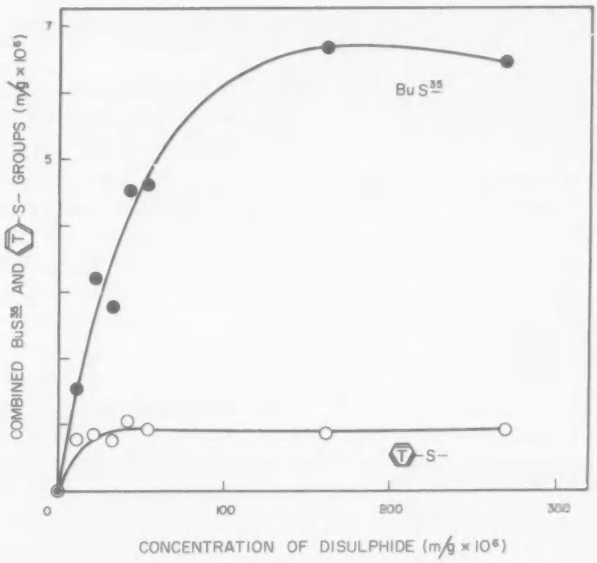



Fig. 1. Influence of concentration of disulfide on the yields of sulphenyl groups combined with polymer.

ters could be favored and consequently a higher concentration of scavenger required to compete with them.

Another implication of the results in Figure 1 stems from the observation of an undiminished yield of radicals in the presence of a relatively large concentration of scavenger. Ordinarily, in radiation chemistry the scavenger concentration is kept very low in order to minimize possible interaction with the precursors of hydrocarbon radicals (charged species, excited molecules, and hydrogen atoms) but these appear to be largely insensitive under the conditions studied here. A subsequent publication will describe the results obtained when similar studies are extended to include still higher concentrations of scavenger by using labeled thiophenol in place of the disulfide.

We gratefully acknowledge that this work was begun in the laboratories of the Natural Rubber Producer's Research Association and that the samples were irradiated at Wantage Research Laboratories (A.E.R.E.).

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# CONFORMATION OF RANDOM COIL MACROMOLECULES IN THE UNDILUTED MOLTEN STATE

It has not, to our knowledge, been noted in polymer literature that there are two conflicting concepts of the conformation of random coiling macromolecules in the molten, undiluted state.

On the one hand, the unperturbed random walk conformation has been inferred (1) from apparently sound thermodynamic reasoning. On the other hand, a "dense volume" conformation has been proposed by E. C. Rochow from study of electron micrographs of replicated fracture surfaces, following a technique called resinography (4). These conformations represent vastly different effective sizes and vastly differing degrees of entanglement between segments of different macromolecules.

As a specific example, consider polyisobutylene of $1 \times 10^6$ molecular weight. From viscometrically observed values of $\overline{r}_0^2/M$ the r.m.s. end-to-end distance (2) is around 760 A. The effective diameter of the coil corresponding to the "physical excluded volume" is according to Tanford (5) about 1.6 times the radius of gyration, thus about 2/3 of the r.m.s. end-to-end distance, which in this example turns out to be about 500 A. According to the Rochow calculation, the diameter D of the polyisobutylene molecule of $M = 1 \times 10^6$ molecular weight, given by $\pi D^3 \rho/6 = M/N_A$ where $\rho$ = bulk density, 0.92 g./cm.$^3$, and $N_A$ = Avagadro number, would be 143 A. More recent resinographic studies by T. G. Rochaw (6) employ the same concepts of "dense volume".

If the Rochow "dense volume" conformation be correct, the interpenetration of segments of neighboring macromolecules in a bulk noncrystalline phase would be limited to a sort of surface layer. In fact, this is explicitly assumed for Rochow writes; "It is a natural assumption that the discontinuities that appear on a fracture surface reflect weaknesses in the cohesion of the structural units, that is, the substance fractures between structural entities . ... It is assumed that the rubber phase breaks by tearing apart such molecules rather than by splitting the molecules themselves." If the unperturbed random coil conformation is correct, interpenetration would occur to an extent differing in order of magnitude, as suggested by the following numerical result. The distance L between centers of mass of the macromolecules can unequivocally be calculated as $L^3 = M/\rho N_A$ giving L = 123 A. for $M = 1 \times 10^6$ and $\rho$ = 0.92. If the domain of one macromolecule as an unperturbed random coil is considered to reside in a spherical volume of $65 \times 10^6$ A.$^3$ (for D = 500 A.), the centers of some 35 other molecules would lie within this domain. This would presumably lead to the results expressed by Flory (3): "Linear polymer chains of high molecular weight normally are almost hopelessly entangled with their neighbors."

Since conformation and the related problem of entanglement are so basic to understanding flow and mechanical properties, it appears that new studies should be made of the subject.

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# INTERMOLECULAR FORCES IN BIAXIALLY ORIENTED POLYMERS

Several years ago Lipatov (1) discussed, in an extensive review, the evaluation of the influence of orientation on the intermolecular forces of polymer chains by comparing the heat of solution of the oriented polymer with that of the unoriented polymer. The heat of mixing Q of a solvent with an amorphous polymer is composed of three components:

$$Q = E_{12} - (1/2)(E_{11} + E_{22}) \quad (1)$$

where $E_{22}$, $E_{11}$, and $E_{12}$ are pair contact energies of polymer-polymer, solvent-solvent, and solvent-polymer bonds respectively. The change in $E_{22}$ upon orientation of the polymer is directly reflected in the change in Q. Results of heat of solution measurements indicate that the intermolecular interaction of polymer chains can increase or decrease upon orientation. We would like to report some preliminary data on the effect of biaxial orientation on the intermolecular forces in polystyrene and polypropylene by the vapor sorption method.

It has been suggested (2) that, in the vapor sorption method, the heat of mixing of a solvent with a crystalline polymer is best written as:

$$Q = E_{12} - (1/2)(E_{11} + E_{22}) + q_{el} \quad (2)$$

where $q_{el}$ is the change in the potential energy of the polymer chain as a result of the change in chain conformation necessary for the accommodation of the vapor molecules. Equation (2) was used to explain the difference between the Q values for the isotactic and amorphous polypropylenes. The inclusion of $q_{el}$ term unfortunately introduces much ambiguity to the interpretation of intermolecular forces from the measurements of heats of sorption. It is customary to assume that only the amorphous region of a semicrystalline polymer is penetrable to vapors. According to the current concept of polymer morphology (3) it appears reasonable to assume that the segments or loops in the amorphous region are not easily "deformed" upon orientation. The probability that each polymer-solvent contact is accompanied by a change in chain conformation is therefore assumed to be the same for both the oriented and the unoriented polymers (i.e., the $q_{el}$ term is assumed to be not affected by orientation.)

Biaxially oriented polystyrene (Kardel) and polypropylene (Cryovac Y) films were used. The crystallinity of the Cryovac film was estimated from the density of the heat-shrunk film to be about 65% (4). In all our calculations, the weight of the polymer refers to the weight of the amor-

phous portion of the material.

The vapor sorption measurements were carried out with a calibrated quartz-spring balance (5). Most of our experiments were conducted at low vapor pressures with relatively small quantities of sorbed vapors. This precaution is necessitated by the observation that disorientation of polystyrene occurs when the solvent content in the polymer increases. The partial molar heat of sorption is calculated from the sorption isotherms by the use of eq. (3):

$$(\Delta\bar{H}_1) = [\partial(\Delta\bar{F}_1/T)/\partial(1/T)]_{N_2} \qquad (3)$$

The value $(\Delta\bar{H}_1)_{N_2 = 1}$ is obtained by extrapolation and is used in subsequent discussions.

The sorption isotherms of benzene and toluene by biaxially oriented PS are shown in Figure 1. Small but positive temperature coefficients were found for the sorption of both vapors. For clarity, only the isotherms at 30°C. are shown. The sorption of toluene by unoriented PS is temperature independent; the amount of sorption reaches about 3 g./100 g. polymer at $P/P_0 \cong .10$ (6). The equilibrium sorption of benzene by unoriented PS at 25°C. is about 2.9 g./100 g. polymer at $P/P_0 = 0.10$ (7). The marked decrease in sorption capacity by biaxially oriented PS is to be contrasted with the increase in sorption of ethylbenzene by oriented PS (presumably uniaxial) (8). Disorientation of biaxially oriented PS occurs during the sorption of toluene at 40°C. and $P/P_0 \cong 0.44$, as evidenced by the shrinkage of the film.

The equilibrium sorption of hexane by biaxially oriented PP is temperature independent while the sorption of benzene increases with temperature. The isotherm for benzene at 40°C. is close to that of hexane and is not shown in Figure 1. The isotherms for the unoriented film are included for the purpose of comparison. The experimental results are summarized in Table I.

In comparing the two PS samples, it may be safely concluded that biaxial orientation causes a decrease in the intermolecular forces which is manifested in the decrease in density and $E_{22}$. The marked reduction in sorption capacity may be ascribed to the decrease in the number of possible configurations of the stretched polymer chains. On the other hand, the loosening of molecular packing appears to be the predominant factor in the observed increase in ethylbenzene sorption by uniaxially oriented PS.

The $\Delta\bar{H}_1$ values for the sorption of hexane and benzene by the two PP samples suggest that the intermolecular forces of the amorphous region of the polymer increases as a result of biaxially orientation. Presumably, this may be interpreted as an indication of an increase in packing density of the amorphous phase upon orientation. Yet the density of the polymer sample as a whole decreases upon biaxial orientation. This

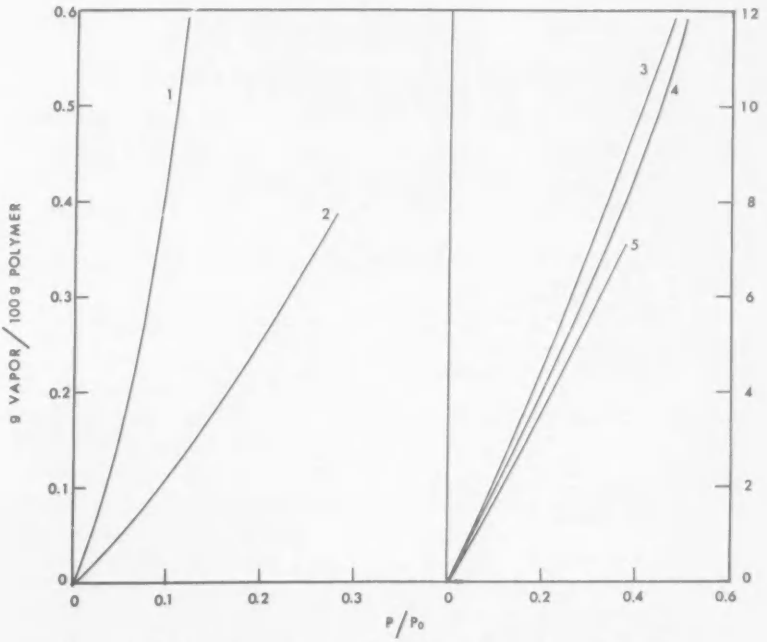


Fig. 1. Sorption of organic vapors by biaxially oriented polymers. Curve 1, benzene – B.O. PS; curve 2, toluene – B.O. PS; curve 3, benzene – U.O. PP; curve 4, hexane – U.O. PP; curve 5, hexane – B.O. PP.

TABLE I

Partial Molar Heats of Sorption

| Polymer | Density g./ml. at 22°C. | Solvent | $(\Delta\bar{H}_1)_{N_2=1}$ cal./mol. |
|---|---|---|---|
| PS | .983 | benzene | ~0 |
| PS (B.O.) | .934 | benzene | 730 |
| PS | | toluene | 0 |
| PS (B.O.) | | toluene | 700 |
| PP (isotactic) | .906 | hexane | 1450 (2) |
| PP (B.O. isotactic) | .903 | hexane | 0 |
| (heat shrunk) | .909 | | |
| PP (isotactic) | | benzene | 2100 (2) |
| PP (B.O. isotactic) | | benzene | 750 |

leads to an interesting postulation that biaxial orientation may have loosened the packing of the crystalline region.

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